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FTIR study of H-bonds cooperativity in complexes of 1,2-dihydroxybenzene with proton acceptors in aprotic solvents: Influence of the intramolecular hydrogen bond

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ABSTRACT

FTIR spectroscopic study of hydrogen bonding of 1,2-dihydroxybenzene (catechol) with proton acc tors has been carried out. The influence of intramolecular and intermolecular hydrogen bonds on strengths of each other in complexes of 1,2-dihydroxybenzene with various proton acceptors has be analyzed. It was shown that intramolecular hydrogen bond is strengthened when 1,2-dihydroxybenze interacts with bases (ethers, amines, nitriles, etc.) in inert solvents. The contribution of the cooperat ity of intramolecular hydrogen bonds in the frequency of stretching vibrations of O–H groups linea depends on the proton acceptor ability of the bases. The solvent effect on hydrogen bond cooperativ in 1,2-dihydroxybenzene–base complexes has been studied. The approach to determine the influe of cooperative effects on the formation of intermolecular complexes with 1,2-dihydroxybenzene proposed. It was shown that the strength of intramolecular hydrogen bonds in the complexes of 1 dihydroxybenzene with bases due to cooperativity of interactions increases by 30–70%, and the stren of intermolecular hydrogen bond by 7–22%.

1. Introduction

Hydrogen bonds (HB) have a significant influence on various physical, chemical and biological processes in condensed matter [1–3]. One of the main properties of hydrogen bonds is cooperativity, which refers to the strengthening of the hydrogen bond in multi-particle complex as compared with the hydrogen bond in complex of 1:1 stoichiometry [4,5]. Cooperative effects play a key role in supramolecular chemistry and biochemistry, and are the reason of association of polar groups in solution, as well as of the processes of molecular recognition [3,6–9].

To date, studies of cooperativity in systems with intermolecular hydrogen bonds, making use of theoretical and experimental methods have been carried out [10–19]. Approaches for assessing the cooperativity factors and the energy of cooperative hydrogen bonding have been developed [5,20–23]. Particularly, multi-particle complexes of monohydric aliphatic alcohols have been thoroughly studied [5,22–31].

Increasing the number of hydroxyl groups in the alcohol molecule creates the possibility of appearance of H-bonded complexes in solution, in which, in addition to the intermolecular interactions, intramolecular hydrogen bonds are formed. Determination of quantitative parameters of cooperative effects in syste with intramolecular hydrogen bonds is an important task, sin such bonds affect the properties of various molecules (e.g., polyo carbohydrates, and polyphenols) in the condensed state [32–35] addition, intra-HB cooperativity affects the conformational state supramolecular receptors such as calixarenes and resorcinarer [36–38].

Intramolecular hydrogen bonds affect the ability of substanc to intermolecular binding. In the work of Kuhn [39] the red f quency shift of the stretching vibration band of the intramolecu H-bonded O–H group of aliphatic diols in an inert solvent w recorded. This shift was caused by the addition of diethyl eth which forms a hydrogen bond with the second hydroxyl group diol molecules. A similar change in the strength of hydrogen bon was found by Spencer et al. [40,41] in the study of complexes catechol and pyrogallol with various bases in carbon tetrachlori Using the infrared spectral data obtained at different temperatur Spencer et al. [40,41] found that the equilibrium constants a enthalpies of hydrogen bonds in these systems are significan greater than in the complexes of phenol. For example, in co plex of tetrahydrofuran with catechol the equilibrium constant a enthalpy is equal to $K = 27.7$ and $\Delta_{HB}H = -8.6$ kcal $\times$ mol^{-1}, wh in the complex with phenol they are $K = 13.5$ and $\Delta_{HB}H = -$ kcal $\times$ mol^{-1}.

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